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TITLE: MASS SPECTROMETRIC STUDY OF LASER DAMAGE IN CALCIUM FLUORIDE

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AUTHOR(S): N. S. Boger, E. C. Apel, and R. C. Estler

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# **Mass Spectrometric Studies of Laser Damage In Calcium Fluoride**

**N. S. Nogar, E. C. Apel and R. C. Estler\***

**Chemical and Laser Sciences Division  
Los Alamos National Laboratory  
Los Alamos, New Mexico 87545**

**\*Permanent Address: Department of Chemistry  
Fort Lewis College  
Durango, Colorado 81301**

Both electron impact- and laser ionization-mass spectrometry have been used to probe the material spalled from  $\text{CaF}_2$  surfaces by the fundamental ( $1.06\mu$ ) and harmonic (355 nm and 266 nm) outputs from a Q-switched Nd:YAG laser. We have identified a number of gas phase products, including Ca, CaF and tentatively,  $\text{CaF}_2$ , and have measured their translational and internal energy distributions.

Our results suggest that while the  $1.06\mu$  experiments can be adequately modeled in terms of a single damage mechanism (likely avalanche breakdown), the short-wavelength results suggest the onset of second mechanism, perhaps multiphoton absorption. This is consistent with both the observed bimodal velocity distribution following short-wavelength damage, and with the decrease in CaF vibrational and rotational excitation.

## **1. Introduction**

Experimental studies of laser induced damage in optical materials have traditionally concentrated<sup>1</sup> on phenomenology of the process: damage thresholds, and physical and bulk material properties effecting these thresholds. More recently, considerable attention<sup>2,3</sup> has been given to the mechanisms responsible for damage, and to the molecular phenomenae associated with the damage process.

In this work we describe a study of the interaction of relatively high-fluence laser pulses ( $\phi \geq 10 \text{ J/cm}^2$ ) with a (nominally) transparent optical medium. We have used both conventional electron impact ionization (with quadrupole mass discrimination) and RIMS (Resonance Ionization Mass Spectrometry) with time-of-flight detection as diagnostics for investigating the sputtered material produced from laser-solid interactions. RIMS<sup>4</sup> is a form of laser-ionization mass spectrometry which takes advantage of available laser-based multiphoton ionization

schemes for the selective detection of atoms and small molecules.  $\text{CaF}_2$  was chosen for this study since it is a common dielectric used in UV and some vis-IR optics, and may be treated as a prototype system for these studies. The objective of this work was to obtain information about the laser-solid interaction through measurement of the chemical and velocity distributions of the particles ejected from the surface during damage.

## 2. Experimental.

All damage experiments were monitored by mass spectrometry, using one of two mass spectrometer/ionization systems: a quadrupole apparatus equipped with electron impact ionization, and a time-of-flight apparatus in which multiphoton photoionization was used. The source region of the quadrupole mass spectrometer (Extrel, C-50) was equipped with an axial ionizer modified<sup>5</sup> to allow the high intensity laser beam to pass through, Fig. 1. Primary ions produced by the damaging laser were detected by turning off the electron impact ionizer, while survey electron impact mass spectra were typically acquired at an energy of 75 eV. A base pressure of  $\leq 1 \times 10^{-8}$  Torr was maintained by an ion pump. The time-of-flight mass spectrometer was modified<sup>6,7</sup> to permit optical access by both the damaging and interrogation laser beams. This latter apparatus was used to measure velocity distributions, and to provide optical spectroscopic identification of the ion precursors. Details have been presented elsewhere<sup>6,7</sup>. A base pressure of  $\leq 1 \times 10^{-7}$  Torr was maintained by a L- $\text{N}_2$  trapped oil diffusion pump.

The  $\text{CaF}_2$  substrates were polished flats (Janoc Optical or Harshaw), 1.9 cm in diameter and 3 mm thick. Each sample was cemented to a 15-cm stainless steel rod for mounting within the mass spectrometer vacuum can. The substrates were placed near (1.5-3 cm) the axis of the mass spectrometer flight tube, and were manipulated by mounting the rods on a rotation-push/pull vacuum feedthrough (Varian Model 1371). The samples were rotated at rates of 1 revolution/15 minutes to 1 revolution/60 minutes, so that a fresh surface was continually exposed to the laser beam.

Optical damage was initiated by either the fundamental (1.06  $\mu$ ), or frequency tripled (355 nm) or quadrupled (266 nm) output of a  $\text{Nd}^{+3}$ :YAG laser (Quanta Ray/Spectra Physics Model DCR 1A). The laser was equipped with filled-beam optics, and produced a beam whose spatial profile is somewhat more sharply peaked than for a gaussian beam. The Q-switched output was 10 nsec FWHM in duration, and smooth within the resolution of our electronics ( $\sim 2$  nsec).

The timing sequence was initiated by the Q-switch synch-out from the YAG laser. When using the quadrupole mass spectrometer, this signal triggered a boxcar averager (PARC 162/164) gated to accept signal from 10-100  $\mu$ sec after the laser pulse. In experiments using the time-of-flight mass spectrometer, the YAG laser synch-out was passed through a variable delay (Tektronix 7904/7B85), a pulse generator (BNC 8010) and then to the trigger of a XeCl excimer laser (Lambda Physics EMG 101). The UV output from this laser was used to pump a tunable dye laser (Lambda Physics FL 2002) which could then probe, via multiphoton ionization, the material spalled by the laser damage event. The identity of the spalled material could be determined by varying the ionization wavelength, while the velocity distribution could be measured

by changing the delay between the damage and interrogation lasers. The boxcar gatewidth for these experiments was 500 nsec, which provides a mass resolution of  $\approx 3$  au.

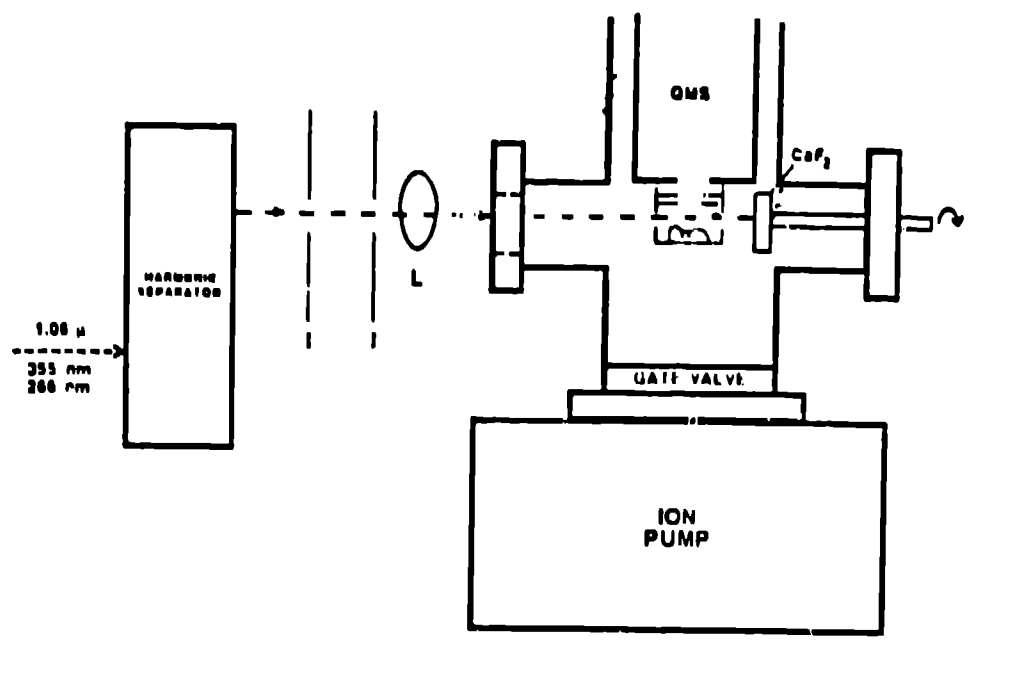


Figure 1. Schematic of the experimental apparatus used for survey mass spectrometry. For details on time-of-flight apparatus, see ref. 7.

### 3. Results

Survey mass spectra were taken with the quadrupole mass spectrometer. Fig. 2 shows the spectrum generated with the electron ionizer turned off. It is dominated by the  $\text{Ca}^+$  peak (40 au), with satellites observed at 42 and 44 due to isotopic variants, and very small contributions due to  $\text{CaF}^+$  (59 au) and  $\text{F}^+$  (19 au). With the electron impact ionizer turned on (75 eV energy), we generated the mass spectrum shown in Fig. 3. This spectrum is the result of a manual background (no laser) subtraction from the observed (laser damage) spectrum. Note the scale change on these figures, which reflects an obvious propensity for the desorption/ablation of neutral species in preference to ions. Even allowing for a reduced detection efficiency for ions formed outside the normal ionization region, we estimate the ratio  $M/M^+$  to be  $\geq 100$ .

The signals observed in Fig 3 can be divided into two types: those originating from the substrate material, and those likely associated with surface contaminants. For the former, a large 40 au peak is again observed, indicative of  $\text{Ca}^+$ . In this case we also observe a substantial peak at 59 au, and a large peak at 19 au. The latter suggests that F atom removal is a high probability process, in agreement with other observation<sup>8</sup>. Although we see no evidence of  $\text{CaF}_2^+$ , this does not mean the  $\text{CaF}_2$  is not being sputtered from the surface. Indeed, a large body of evidence<sup>9-10</sup> suggests that  $\text{CaF}_2$  is the dominant thermal evaporant. The reason for our non-observation of

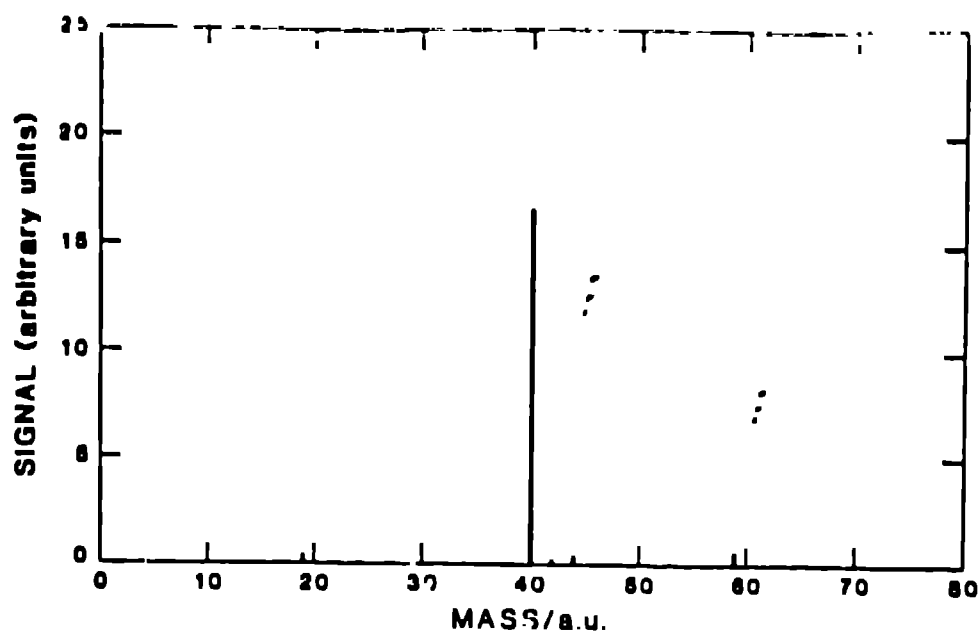


Figure 2 Survey mass spectrum of primary ions (no electron impact ionizer) produced by 266 nm damage on  $\text{CaF}_2$  at  $15 \text{ J/cm}^2$  (10 nsec pulse)

$\text{CaF}_2^+$  is that electron impact ionization<sup>11,12</sup> produces predominately  $\text{CaF}^+$ , and, at higher energies,  $\text{Ca}^+$  from the parent molecule. The observed  $\text{CaF}^+$  and  $\text{Ca}^+$  signals are thus likely due to both direct ionization of Ca and CaF (see below), and to combined ionization/fragmentation of  $\text{CaF}_2$ . A number of other minority species ( $\leq 1\%$ ) can be observed at higher sensitivity, and are largely consistent with previous observations<sup>13</sup>.

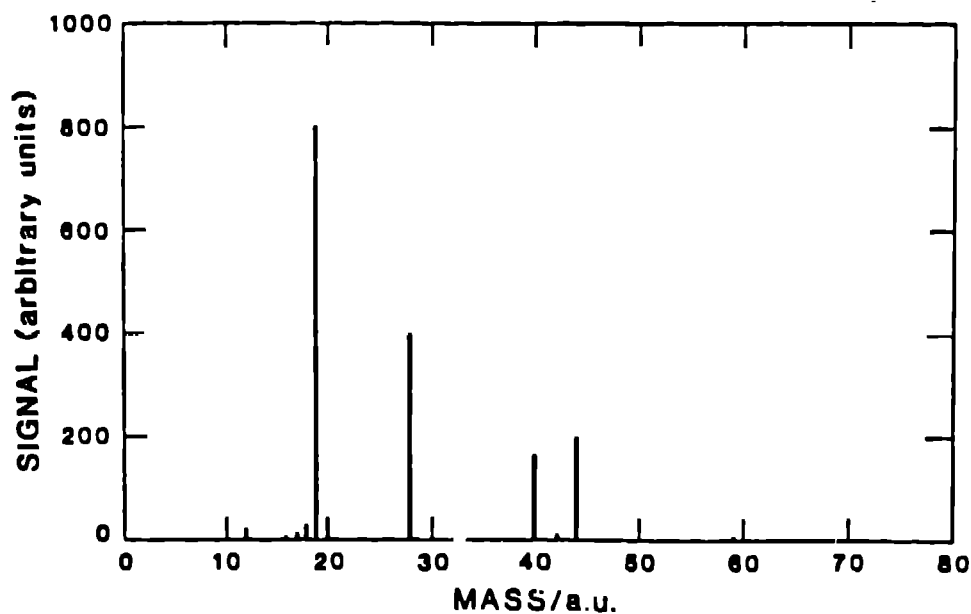


Figure 3. Survey mass spectrum of neutral species (ionized by electron impact) spalled from the  $\text{CaF}_2$  surface. Conditions identical to Fig. 2.

Among the impurities routinely observed in the electron impact mass spectra are a large peak at 44 au, presumably  $\text{CO}_2$ , a peak at 28 due to CO (or  $\text{N}_2$ ), the water group at 16, 17 and 18 au, and a very weak signal at 12 au. We have not determined the identity of this last constituent, but it is a frequently observed signal in this apparatus. These results are consistent with the known<sup>14,15</sup> tendency of water to adsorb on  $\text{CaF}_2$  surfaces.

Results from the laser damage/laser ionization experiments in the ToF mass spectrometer yield significant additional information. First, since the multiphoton ionization process is resonantly enhanced, the excitation (ionization) spectrum can be used to determine the precursor for a particular ion. And second, by varying the time delay between the damage and interrogation pulses, the velocity distribution of the spalled material can be obtained.

The  $\text{Ca}^+$  observed in the laser ionization experiments is produced from atomic Ca by a "2+1" (photons to resonance + photons to ionize) process<sup>7</sup> through the enhancing  $^1\text{P}_0^0$  state at  $37298\text{ cm}^{-1}$ . Similarly, the  $\text{CaF}^+$  observed in this set of experiments is derived from CaF by a 2+1 ionization process through the  $\text{F}^2\Pi$  state ( $T_0=37550\text{ cm}^{-1}$ ). These particular ionization paths were chosen so that both species could be detected with the same laser dye. While these results indicate that at least some of the ablated material is directly spalled as Ca and CaF, we have no direct evidence as to what fraction spalls as fragments, and what fraction as  $\text{CaF}_2$  molecules. Neither the previously mentioned electron impact spectra, nor the optical ionization currently under discussion is sensitive to  $\text{CaF}_2$ . We can only infer from thermal vaporization studies<sup>9,10</sup> that a substantial fraction is likely to evaporate as molecules.

Additional information was obtained by measuring both the internal and translational energy distribution of the the spalled Ca and CaF. Velocity distributions were measured by varying the time delay between the damage and ionization (probe) lasers. The internal energy content of the CaF radicals was probed by varying the wavelength of the ionization (dye) laser, so that an excitation spectrum was obtained. Damage was initiated at the fundamental ( $1.06\mu$ ), and frequency tripled (355 nm) and quadrupled (266 nm) wavelengths. The results were found to be dependent on wavelength and may be summarized<sup>7</sup> as follows:

- a. For  $1.06\mu$  irradiation, we observed thermal (850 K) velocity distributions for both Ca and CaF. In addition, the CaF radical exhibited significant amounts of internal (rotational and translational) excitation, consistent with an internal "temperature" of  $\sim 10^3\text{K}$ .
- b. For both 355nm and 266nm irradiation, the velocity distributions were bimodal, Fig. 4, with a fraction ( $\leq 50\%$ ) of the spalled material exhibiting very high (4000 K) kinetic temperatures, while the remainder exhibited a temperature similar (800-1000 K) to that observed for the  $1.06\mu$  experiments. Note that the flight times exhibited in Fig. 4 are for optical time-of-flight (from  $\text{CaF}_2$  surface to interrogation zone) and not the flight time in the mass spectrometer flight tube. In addition, both the vibrational and rotational temperatures of the CaF radicals decreased with decreasing damage wavelength.

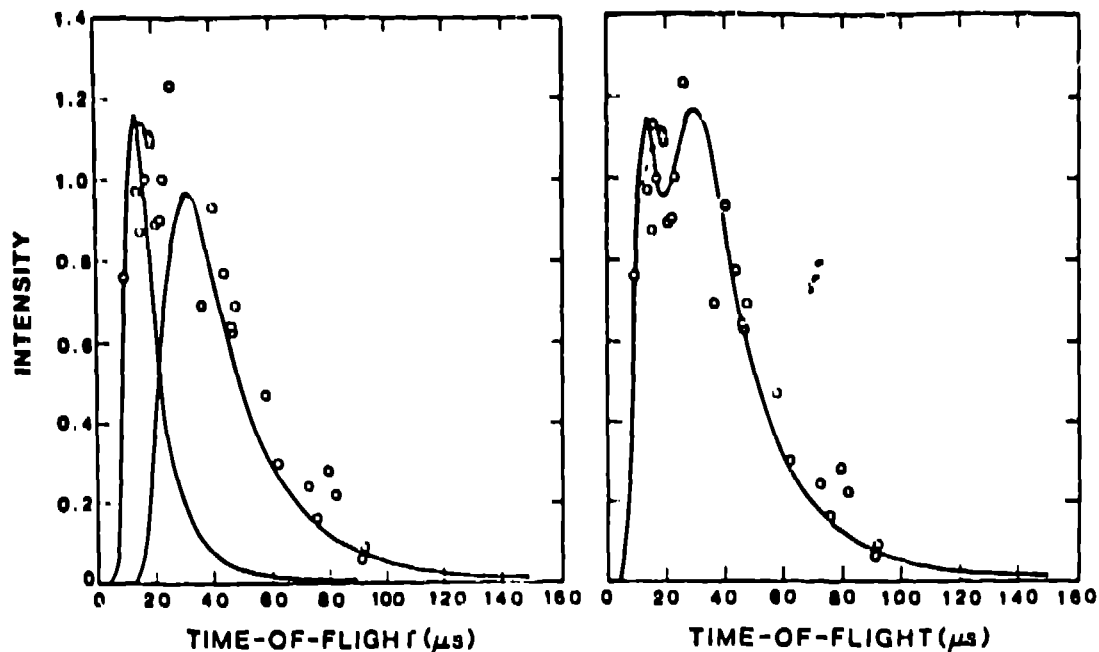


Figure 4. Optical time-of-flight distribution (o) for Ca spalled from  $\text{CaF}_2$  surface at 266 nm,  $15 \text{ J/cm}^2$ : a) shows individual fast (4000K) and slow (850K) components for comparison with data, b) shows overall composite fit of fast (33%) and slow (67%) components.

#### 4. Discussion

In regard to the characterization of the process of laser sputtering, or laser damage, the terms "thermal" and "electronic" have been used to describe different mechanisms of particle ejection from substrate surfaces in the hope of categorizing the numerous possible processes<sup>16</sup>. Thermal normally implies vaporization from a transiently heated surface, while electronic sputtering refers to a collection of processes commonly associated with the creation of electronic defects eventually leading to particle ejection. Such defects might include those resulting from direct interaction of the incident light with a surface atom or diffusing defects such as hole pairs. Such processes often lead to sudden bond rupture, and may lead to highly nonthermal velocity distributions in the ejected particles<sup>17</sup>. Indeed, the observation of nonthermal energy distributions have been used to infer the existence of a number of laser-material interactions<sup>18</sup>, including direct photodissociation and ejection of surface material<sup>19</sup>. It is important to note, however, that some electronic sputtering mechanisms do lead to ejected particles with thermal velocity distributions<sup>20</sup>.

Our results do not necessarily point to a single mechanism in the initiation of the breakdown event, but are significant from the standpoint that a change in mechanism, i.e., an opening of a second channel at high photon energy, is indicated. The kinetic temperatures and qualitatively similar estimates of the CaF internal energies observed at  $1.08\mu$  argue for a thermal or sonic mechanism, possibly initiated by avalanche breakdown. In addition, it is tempting to speculate that absorption at this long wavelength is due to a physical or chemical defect in the substrate, since direct excitation of the crystal would imply simultaneous absorption of a large number of photons. The results at shorter wavelengths suggest a more direct photophysical interaction, where rapid energy deposition is followed by non-adiabatic transitions of the fragments to antibonding states<sup>19,21</sup>. Such a mechanism can lead to the nonequilibrium of the various degrees of freedom observed here and also to a nonisotropic angular distribution of products.

## 5. References

- [1] Ready, J. F. Effects of High-Power Laser Radiation, New York, Academic, 1971.
- [2] Smith, W. L. Laser-Induced Breakdown in Optical Materials. Opt. Engin. **17**; 489-503; (1978).
- [3] Kelly, R.; Cuomo, J. T.; Leary, P. A.; Rothenberg, J. E.; Braren, B. E.; Allotta, C. F. Laser Sputtering Part I. On the Existence of Rapid Laser Heating at 193 nm. Nucl. Instr. and Meth. **B9**; 329-340; 1985.
- [4] Nogar, N. S.; Estler, R. C.; and Miller, C. M. Pulsed Laser Desorption for Resonance Ionization Mass Spectrometry. Anal. Chem. **57**; 2441-2444; 1985.
- [5] Estler, R. C.; and Nogar, N. S. Mass Spectrometric Identification of Wavelength Dependent UV-Laser Photoablation Fragments from Polymethylmethacrylate. Appl. Phys. Lett.; in press.
- [6] Estler, R. C.; Nogar, N. S. Investigation of Optical Damage via Resonance Ionization Mass Spectrometry. Proceedings of the Symposium Laser Induced Damage in Optical Materials; 1985. In press.
- [7] Estler, R. C.; Apel, E. C.; Nogar, N. S. Laser Mass Spectrometric Studies of Optical Damage in CaF<sub>2</sub>. J. Opt. Soc. Am. B., In press (1987).
- [8] Hayes, W.; Lambourn, R. F. Production of F and F-Aggregate Centres in CaF<sub>2</sub> and UO<sub>2</sub> by Irradiation. Phys. Stat. Sol.; **57**, 633-699; 1973.
- [9] Himpfel, F. J.; Karlsson, U. O.; Morar, J. F.; Rieger, D.; Yarmoff, J. A. Determination of Interface States for CaF<sub>2</sub>/Si(111) from Near-Edge X-Ray-Absorption Measurements. Phys. Rev. Lett. **56**; 1497-1500; 1986; Karlsson, U. O.; Morar, J. F.; McFeely, F. R.; Rieger, D.; Yarmoff, J. A. Formation of a New Ordered Structure of CaF<sub>2</sub>/Si(111) by Ultraviolet Irradiation. ibid. **57**; 1247-1250; 1986.

- [10] Blue, G. D.; Green, J. W.; Bautista, R. G.; Margrave, J. L. The Sublimation Pressure of Calcium(II) Fluoride and the Dissociation Energy of Calcium(I) Fluoride. *J. Phys. Chem.* **67**; 877-882; 1963.
- [11] Hildebrand, D. L.; Murad, E. The Dissociation Energy of Boron Monofluoride from Mass-Spectrometric Studies. *J. Chem. Phys.* **43**; 1400-1403; 1965; Mass-Spectrometric Determination of the Dissociation Energy of Beryllium Monofluoride. *Ibid.* **44**; 1524-1529; 1966.
- [12] Farrow, R. F. C.; Sullivan, P. W.; Williams, G. M.; Jones, G. R.; Cameron, D. C. MBE-Grown Fluoride Films: A New Class of Epitaxial Dielectrics. *J. Vac. Sci. Technol.*; **19**; 415-420; 1981.
- [13] Buhl, R.; Preisinger, A. Crystal Structures and their Secondary Ion Mass Spectra. *Surf. Sci.* **47**; 344-357; 1975.
- [14] Pallik, E. D.; Gibson, J. W.; Holm, R. T. Internal-Reflection Spectroscopy Study of Adsorption of Water on  $\text{CaF}_2$  Surfaces. *Surf. Sci.* **84**; 164-178; 1979.
- [15] Allen, S. D.; Porteus, J. O.; Faith, W. N.; Franck, J. B. Contaminant and Defect Analysis of Optical Surfaces by Infrared Laser Induced Desorption. *Appl. Phys. Lett.* **45**; 997-999; 1984.
- [16] Rothenburg, J. E.; Kelley, R. Laser Sputtering Part II: The Mechanism of the Sputtering of  $\text{Al}_2\text{O}_3$ . *Nucl. Instr. Meth.* **B1**; 291-300; 1984.
- [17] Madey, T. E. Electron- and Photon-Stimulated Desorption: Probes of Structure and Bonding and Surfaces. *Science* **234**; 316-322; 1986.
- [18] Levine, L. P.; Ready, J. F.; Bernal, E. G. Production of High-Energy Neutral Molecules in the Laser-Surface Interaction. *IEEE J. Quant. Elec.* **QE-4**; 18-23; (1968).
- [19] Bjourdon, E. B. D.; Cowin, J. P.; Harrison, I.; Polanyi, J. C.; Segner, J.; Stanners, C. D.; Young, P. A. UV Photodissociation and Photodesorption of Adsorbed Molecules. 1.  $\text{CH}_3\text{Br}$  on  $\text{LiF}(001)$ . *J. Phys. Chem.* **88**; 6100-6103; 1984.
- [20] Stoffel, N. G.; Riedel, R.; Colavits, E.; Margaritondo, G.; Haglund, R. F.; Tagliener, E.; Tolk, N. H. Photon-Stimulated Desorption of Neutral Sodium from Alkali Halides Observed by Laser-Induced Fluorescence. *Phys. Rev.* **B32**; 6805-6808; 1985.
- [21] Jost, B.; Schueler, B.; Krueger, F. R. Ion Formation from Alkali Halide Solids by High Power Pulsed Laser Irradiation. *Z. Natur-Forsch.* **37a**; 18-27; 1982.